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## **NOVEL DUPLEX VAPOR- ELECTROCHEMICAL METHOD FOR SILICON SOLAR CELLS**

By: L. Nanis, A. Sanjurjo, K. Sancier

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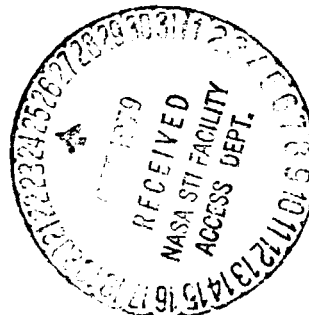
Prepared for:

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Attention: Dr. Ralph Lutwack, Spacecraft Power Station

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SRI Project PYU 4980



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R. W. Bartlett, Director  
Materials Research Laboratory



## SUMMARY

The  $\text{SiF}_4$ -Na reaction system has been scaled up to a reactor i.d. of 13 cm; the capacity of the Na chip feeder has also been increased. The system can now produce 5-kg batches of reaction product (mixed Si and NaF) at a production rate of 1.2 kg Si per hour.

The melt-separation system has been modified to routinely melt 5-kg batches of mixed reaction product fed in a continuous mode at a production rate of 0.5 kg Si per hour.

Support studies of Si coalescence show NaOH may be added to the NaF melt in amounts up to 5 wt% before there is any tendency for the Si to form large drops rather than a single pool.

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## PREFACE

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program aimed at the development of low-cost solar arrays. The work reported here was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

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## TASK 1

### $\text{SiF}_4$ -Na REACTION

#### A. Solid Na Feed

Current work on the reaction between gaseous  $\text{SiF}_4$  and solid Na has proceeded with the following objectives:

- Obtain data needed for plant design by scaling up the reaction to produce greater amounts of reaction product.
- Increase reaction rate and overall Si production rate.
- Increase the efficiency of the reaction so that less unreacted Na and less  $\text{Na}_2\text{SiF}_6$  are produced.
- Produce large amounts of reaction product for use in studies of Si recovery by melt separation (Task 2).

The progress made toward attaining the above objectives can best be discussed in terms of the development work on a scaled-up reactor. The effects of reactor scale-up on reactor performance are summarized in Table 1. An advantage demonstrated by increasing the reactor to its present size (13 cm i.d.) is the increased production rate compared with the previous 7-cm reactor. Of special significance is the large decrease in residual Na in the reaction product. As shown in Figure 1, the improvement in Na utilization may be seen by examining the effect of the sodium addition rate on the amount of unreacted sodium in the reaction products. In all runs, the reactor was maintained at a minimum temperature in the range of 400°C to 450°C. The results for the 7-cm reactor were taken from the work reported in our Quarterly Report No. 13. In that report, we ascribed the difference in the behavior of sodium when fed as slices and chips to differences in the surface-to-volume ratio of the sodium; that is, the greater this ratio, the faster and more complete the reaction. In the 13-cm reactor, unreacted sodium was not detectable, even for a sodium-addition rate of about 14 g Na/min. By comparison, the 7-cm reactor would have to be operated at a rate less than about 2 g Na/min to achieve complete reaction of the sodium.



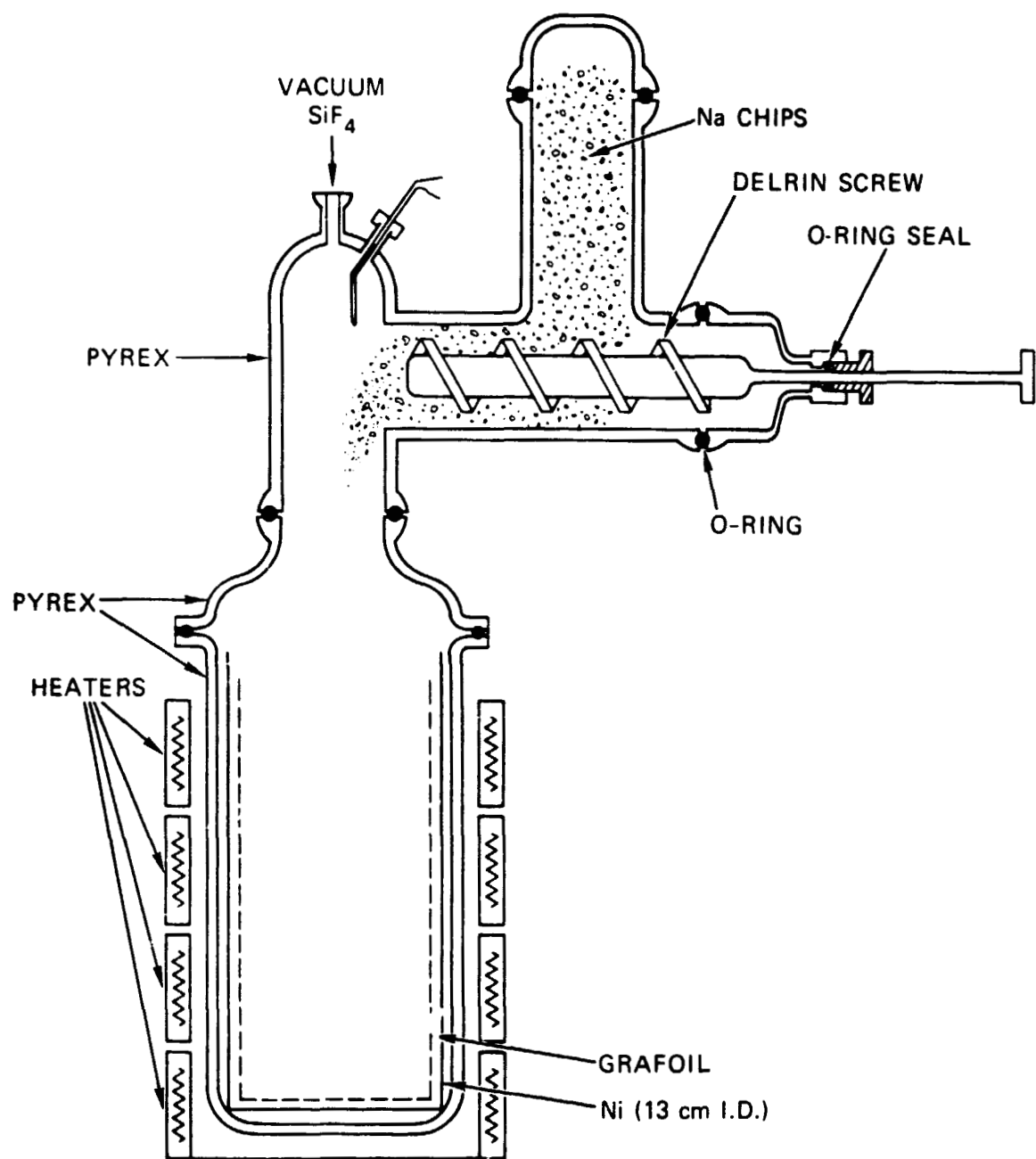
Table 1

## EFFECT OF SCALE-UP ON REACTOR PERFORMANCE

<u>Reactor Characteristic</u>	<u>7-Cm Reactor</u>	<u>13-Cm Reactor</u>
Design parameter		
Diameter, cm	7	13
Height, cm	60	60
Sodium dispenser capacity		
Slices, kg/filling	1.3	-
Chips, kg/filling	0.35	0.7
Pellets, kg/filling	0.85	-
Performance <sup>a</sup>		
Reaction product, kg/batch	1.5	5.0
Silicon, kg/batch	0.15	0.5
Reaction rates, kg Si/hr	0.1	1.2
Unreacted sodium wt%	10	0

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<sup>a</sup>Reactor temperature 400°C, Na chip feed.



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FIGURE 1 13-cm REACTOR FOR THE  $\text{SiF}_4$ -Na REACTION: SOLID Na FEEDING TECHNIQUE

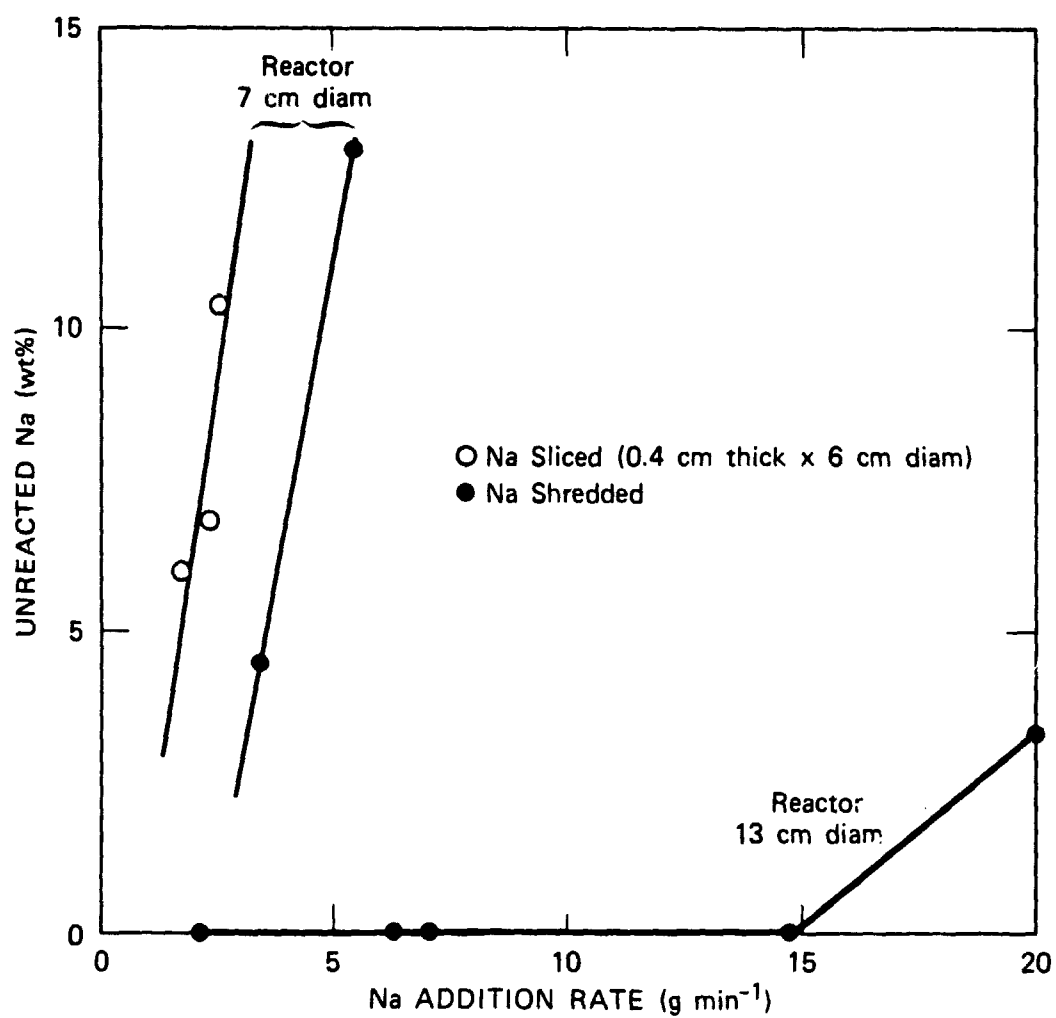
The better performance of the larger reactor is undoubtedly due to the higher temperature of the reaction zone; the higher temperature promotes a faster and hence a more complete reaction between the  $\text{SiF}_4$  and the sodium. This higher temperature is a consequence of the small ratio of reactor surface to reactor product volume in the larger reactor. In further scale up, we expect that the higher reaction temperature achievable in larger reactors will have the following advantages:

- Much higher sodium-addition rate will be possible, with complete utilization of sodium.
- The higher reaction temperature will increase the efficiency of silicon production by decreasing the tendency to form  $\text{Na}_2\text{SiF}_6$  as a by-product.

#### B. Reactor Design

The design of the new 13-cm reactor is shown in Figure 2. In addition to its larger size, the new reactor differs from the 7-cm reactor (Quarterly Report No. 13 page 4) in two ways: (1) the sodium dispenser was enlarged and modified to provide for gravity feed rather than pushing the sodium upward, and (2) the interior glass surfaces of the dispenser were coated with a thick layer of epoxy resin to prevent metallic contamination of the sodium. Experience gained with the plastic screw feeder shown in Figure 1 indicated excellent performance when the feeder was working properly but also revealed a tendency for the feeder to jam whenever the malleable sodium accidentally lodged in the space between the Pyrex wall and the outer thread of the Delrin screw. Although this feed technique is attractive because it lends itself to automation, studies to improve the technique were postponed in favor of a simpler procedure. The central horizontal rod was retained, the plastic screw was completely removed, and a plastic "hoe" blade was attached to the rod. The blade readily permitted normal control for feeding sodium chips to the reactor at a constant rate.

As described in Quarterly Report No. 13, when Na slices were fed to the reactor one at a time, the sodium addition rate was controlled by allowing enough time for the  $\text{SiF}_4$  pressure to return to 1 atm, thus indicating completion of the reaction. In the 13-cm reactor, Na is being



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FIGURE 2 EFFECT OF Na ADDITION RATE AND REACTOR DIAMETER ON AMOUNT OF UNREACTED Na.

Reactor temperature 400-450°C.

fed to the reactor only in chip form at a constant rate so that the  $\text{SiF}_4$  flow rate was maintained at a constant value, typically 2.8 liters  $\text{SiF}_4$ /min. The  $\text{SiF}_4$  flow rate was measured with an electronic flowmeter (Precision Flow Devices, Model PFD-112, maximum flow rate of 10 liters/min). The total volume of  $\text{SiF}_4$  flowing to the reactor was obtained by feeding the output of the electronic flowmeter to an electronic integrator (Tylan Corporation, Model FMT-3) and recording the output of the integrator.

#### C. Sodium Preparation

The sodium chips were prepared by feeding 0.5-lb (225 g) blocks of sodium (6-cm-diameter rod cut longitudinally) to a food processor using a blanket of argon to minimize contact with atmospheric oxygen and moisture. Two food processors were used for chipping the sodium. Initially, a kitchen processor (Hamilton Beach) with a grating attachment was used to prepare the chips. The food processor chopper attachment was then used to make pellets from the chips. For use in the scaled-up reactor, we used a heavy-duty food processor (Robot Coupe) with either of two grating attachments: "carrot" for fine chips and "cole slaw" for coarse chips. The size and shapes of the sodium chips prepared in the food processors are shown in Figure 3.

#### D. Reactor Procedure

The procedure used for a typical run with the 13-cm reactor is as follows:

1. The Pyrex reactor is assembled with an inner nickel liner (13 cm diam. x 60 cm) which is, in turn, lined with sheet Grafoil.
2. About 60 g of NaF is then added to the bottom of the reactor to prevent the reaction products from adhering to the Grafoil.
3. The sodium chips (~ 600 g) are transferred to the vertical dispenser while argon flows through the apparatus and out through the top of the open dispenser.

### HAMILTON BEACH PROCESSOR

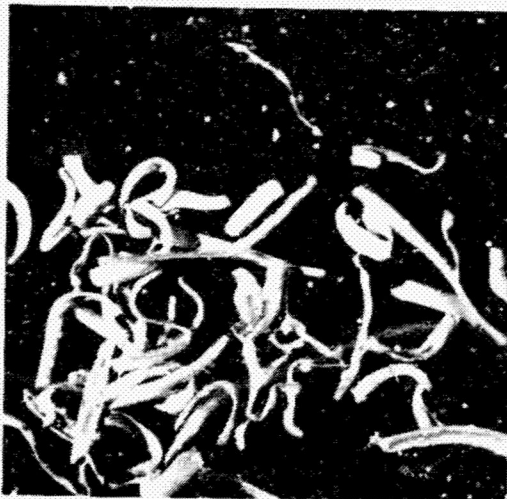


Grated



Pelletized

### ROBOT COUPE PROCESSOR



Carrot Grater



Cole Slaw Grater

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FIGURE 3 SHAPE OF SODIUM CHIPS PREPARED IN FOOD PROCESSORS

4. The apparatus is evacuated while the reactor is heated, along its length (80 cm), to a given temperature, typically 400°C.
5.  $\text{SiF}_4$  gas is admitted through a low-pressure regulator; gas pressure is controlled at about 1 atm.
6. The sodium chips are added to the hot reactor; they ignite immediately as indicated by the  $\text{SiF}_4$  flow rate. The chips are added so that the  $\text{SiF}_4$  flow rate is constant, typically 2.8 liters/min. The largest flow rate that we used (3.6 liters  $\text{SiF}_4$ /min) produced so much heat that the Pyrex reactor envelope softened and the run had to be terminated.
7. About 10 min after all of the sodium has been added, the  $\text{SiF}_4$  flow is stopped and the apparatus is evacuated and allowed to cool.
8. The reaction product is removed from the reactor, crushed with a plastic hammer, and most (but not all) of any adhering Grafoil is removed.
9. The reaction product is analyzed for residual sodium by an acid titration procedure.

The solid Na chips in the dispenser will not react with the  $\text{SiF}_4$  gas since the dispenser is at room temperature; however, two precautions are routinely observed. The  $\text{SiF}_4$  is added slowly to prevent local heating of the sodium due to the heat developed by the reaction between  $\text{SiF}_4$  and water adsorbed on the sodium. Such local heating can be sufficient to initiate the reaction between  $\text{SiF}_4$  and the sodium. In one run in which the  $\text{SiF}_4$  was added rapidly, the Na was ignited in the dispenser (it was readily extinguished by evacuating the  $\text{SiF}_4$ ).

Experience with reactor operation has also shown that over-filling of the reactor with the reaction products should be avoided; overfilling can cause the hot reaction zone to come too close to the sodium chips in the horizontal (transfer section) of the sodium dispenser. In one experiment, Na ignited in the  $\text{SiF}_4$  atmosphere in the horizontal feed section when the reaction products had built up unevenly on one side of the reactor to a height of 67 cm (7 cm above the nickel liner).

#### E. Future Plan

Future work will proceed along two lines. First, the 13-cm reactor will be used to produce reaction products for melt separation and to evaluate the kinetics of the reaction at this stage of scale-up. Second, an Inconel metal reactor (18 cm diameter) is under construction and it will be used to evaluate the results of scaling up cross-section area twofold. The planned 18-cm metal reactor will have a capacity of 1 kg Si per batch and will allow operation at elevated temperatures. Also, methods are under development for rapid analysis of silicon and  $\text{Na}_2\text{SiF}_6$  contained in the reaction products.



## TASK 2

### MELT SEPARATION

#### A. Modes of Operation

The main goal of Task 2 is to develop a system capable of continuous melting of reaction product produced by the  $\text{SiF}_4$ -Na reaction (Task 1) for the separation of Si and NaF into two distinct phases. The development of melt separation has been staged in modes of increasing complexity. These modes are

- Batch loading and melting of reaction products.
- Loading (feeding) continuously and melting in a batch mode.
- Loading and melting continuously with intermittent discharge of liquid Si and liquid NaF.

The first two modes were carried out with kilogram-quantities of reaction product in the converted crystal growing furnace (Quarterly Report 13). The first scaled-up experiments were run with reaction product obtained during exploratory studies of the  $\text{SiF}_4$ -Na reaction in which the amount of unreacted Na and  $\text{Na}_2\text{SiF}_6$  were unusually high (up to 10% of Na and 20% of  $\text{Na}_2\text{SiF}_6$ ). The fact that the Si sometimes did not coalesce into one pool prompted auxiliary studies, described in Sec. 2.B, to determine the effect of sodium oxidation products. These oxidation products occur where residual sodium in the reaction product combines with atmospheric oxygen and water vapor prior to melting.

In the batch load and melt mode, 1.5 kg of reaction product was loaded in a 6 in. i.d. x 8 in. (15.2 cm i.d. x 20.1 cm) graphite crucible and heated to 1200°C for 30 min in  $\text{SiF}_4$  gas atmosphere. This atmosphere was provided to react with previously unreacted sodium in the reaction product, thus keeping the sodium from attacking the graphite. In order to achieve complete melting, the crucible was heated to  $1450 \pm 20^\circ\text{C}$  for 30 min. A cross section of the crucible after melting showed that Si had melted and agglomerated in small spheres (0.1 to 1.0 cm in. diameter) on the bottom of the reactor. The NaF was on top of the Si, as

expected, but had a hard earthy consistency unlike that of pure NaF; however, only NaF was detected by x-ray analysis.

In the continuous-feed batch-melt mode, 1.5 kg of product mixture was initially loaded into the graphite crucible and 1.7 kg of the same product mixture was loaded into the product feeder (see Quarterly Report No. 13 for operating details). The crucible was heated to 1200°C in an  $\text{SiF}_4$  atmosphere to melt the NaF already in the crucible. At that temperature, the products stored in the feeder were added to the crucible continuously for 15 min. To melt the silicon, the temperature was then raised to  $1450 \pm 20^\circ\text{C}$  for 15 min. The results obtained were similar to those described for the batch feed melt mode. The separation of phases was good but instead of coalescing into a large pool, silicon formed several discrete spheres. In more recent production of reaction product in Task 1, the reaction of Na has been complete. When Na-free reaction product is melted, the Si consistently coalesces into a large pool.

With Na-free reaction product and the continuous-feed batch-melt mode in a crucible maintained under argon atmosphere at  $1450 \pm 20^\circ\text{C}$ , batches of reaction products of up to 4.5 kg were melted and Si separation was achieved during the quarter. Part of the reaction product (2 kg) was loaded in the crucible, and part was loaded in the side arm feeder. After the crucible load had been maintained at  $1450^\circ\text{C}$  for 5 min, the balance of the reaction product was added in 0.2-kg increments at intervals of 3 min. At that rate, the added reaction product had time to completely melt before the next addition, as determined by observation through the upper window of the feeder. After the last addition, the temperature was raised to  $1490 \pm 20^\circ\text{C}$  for 5 min and then the furnace was turned off. The quenched Si and NaF were extracted from the crucible; a cross section showed good separation between both phases.

In both the batch feed and melt studies and the continuous feed and melt studies, high purity Si was obtained. According to our readily

available analytical methods, all impurity elements were below the detection limits of emission spectrographic analysis. Techniques of sample preparation and standard calibration are presently being developed for plasma emission spectrography. This method has lower detectability limits than conventional emission spectrography and will be used for improved routine analysis and for cross-checking the results of spark source mass spectrometry.

Weight losses during melting were small (less than 15 wt%) and were mostly due to thermal decomposition of  $\text{Na}_2\text{SiF}_6$  to NaF and volatile  $\text{SiF}_4$ . As mentioned in Sec. 1D, the use of metal reactors in the  $\text{SiF}_4$ -Na reaction will avoid the  $\text{Na}_2\text{SiF}_6$  formation so that weight loss due to  $\text{Na}_2\text{SiF}_6$  will be negligible. The vaporization of NaF and the vapor transport of Si were negligible (less than 2 wt%). The NaF and Si are deposited in the cooler region of the graphite crucible and pipe. In principle, both can be recovered simply by occasional heating of the pipe above the melting point of Si, although our present experimental melting apparatus is not set up to do this. With these procedures, yields close to 100% were obtained by melting reaction products free of unreacted Na.

#### B. Silicon Coalescence Studies

The tendency of Si to agglomerate into several globules instead of one pool, when using reaction products that contained unreacted Na and that had been stored in air prior to melting, prompted auxiliary experiments in an effort to understand this behavior. The auxiliary melting experiments were carried out in a small induction furnace. It was clearly established from the results that complete coalescence occurs when the reaction products are free of unreacted Na. The cause of partial coalescence was suspected to be the presence of compounds formed when unreacted Na was exposed to air and moisture. Expected compounds include  $\text{Na}_2\text{O}$ , NaOH,  $\text{SiO}_2$ , and  $\text{Na}_2\text{SiO}_3$ . Diagnostic experiments were performed to determine the effect on Si coalescence produced by these compounds when they are present in the reaction product. A sodium-free reaction product that had shown good Si coalescence was mixed with each of the above-mentioned compounds. The mixture was heated to

20°C for 5 min, following the same temperature-time profile that had resulted in complete coalescence of the Si in the original sodium-free reaction products.

The results, shown in Table 2, indicate that the presence of more than 10 wt% of any of the compounds, NaOH, SiO<sub>2</sub>, or Na<sub>2</sub>SiO<sub>3</sub>, in the reaction product will cause formation of several Si globules rather than one complete Si pool. It may be expected that at 1450°C the Na<sub>2</sub>SiO<sub>3</sub> formed from the reaction of Si or SiO<sub>2</sub> with Na<sub>2</sub>O or NaOH may further react with NaF to produce fluoro-oxysilicate species. The presence of such species adsorbed on the Si droplet surface may hinder droplet coalescence. For the melt separation system that will utilize continuous feed of reaction product with an intermittent tapping mode, a large pool of Si at the bottom of the crucible is desired. Partial coalescence into Si globules will not be a problem for this mode when the Na-free reaction products now being produced in Task 1 are used.

Table 2

## SUMMARY OF COALESCENCE EXPERIMENTS

<u>Composition (wt%)</u>	<u>Coalescence</u>
(Si + 4NaF)	Complete
(Si + 4NaF) + 4% NaOH	Complete
(Si + 4NaF) + 10% NaOH	Complete
(Si + 4NaF) + 20% NaOH	Incomplete
(Si + 4NaF) + 10% Na <sub>2</sub> SiO <sub>3</sub>	Incomplete
(Si + 4NaF) + 10% SiO <sub>2</sub>	Incomplete